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Prediction of Uranium Transport in an Aquifer at a Proposed Uranium *In Situ* Recovery Site: Geochemical Modeling as a Decision-Making Tool

Raymond H. Johnson, Bronwyn P. C. Grover and Hlanganani Tutu

Additional information is available at the end of the chapter

Abstract

Roll fronts are some of the most important uranium deposits and are quite common in the United States. Generally, a roll front has an oxidized zone and a reduced zone, the latter being the zone of high mineralization and a target for *in situ* recovery (ISR) mining. The challenge remains the gathering of information to enable making informed decisions regarding post-mining groundwater quality. In this study, potential uncertainties in uranium sorption on iron oxyhydroxides or hydrous ferric oxides (HFO) following mining were assessed, as these oxidized zones create a greater risk for future uranium transport than fully reduced zones. Using two different geochemical databases, uncertainties in predicting uranium sorption on HFO based on a post-recovery restoration scenario were studied. The scenario was assessed using one-dimensional PHREEQC geochemical modeling simulations with respect to: uranium, oxygen, carbon dioxide, and iron hydroxide concentrations. The results of the simulations showed that uranium concentrations in solution are likely to be controlled by the amount of HFO available for sorption and the concentration of uranium-carbonate complexes formed in the solution. The presence of calcium, through the dissolution of calcite, was found to reduce the adsorption of uranium onto HFO as the resulting uranium-calcium-carbonate complexes are quite soluble. Overall, the simulations provide a procedure for predicting down-gradient uranium concentrations based on ultimate restoration levels at uranium ISR sites. This is important for risk assessment, regulatory enforcement, and decision making.

Keywords: hydrous ferric oxides, *in situ* recovery, reactive transport modeling, uranium, PHREEQC

1. Introduction

Uranium is a toxic element due to its radioactivity and chemical toxicity. In the environment, it exists as the soluble uranyl ion, UO_2^{2+} (U(VI)) and the reduced form U(IV). The oxidized form is capable of forming complexes with ligands such as chlorides, fluorides, phosphates, nitrates, sulfates, selenides, tellurides, carbonates, and organic moieties, and these influence its speciation and transport[1–4]. The toxicity and bioavailability of uranium is dependent on its speciation upon uptake as well as changes in speciation during transport in the human body [5]. Ingestion of uranium in drinking water has been shown to negatively affect the kidneys, causing their inflammation, a condition called nephritis [5, 6]. It can also affect the bone marrow by replacing calcium, thereby weakening the bones and causing osteoporosis [4].

In the United States, roll fronts are important deposits of uranium. These deposits develop as groundwater containing uranium species migrates through porous and permeable sandstone or conglomerate aquifers (**Figure 1**). Groundwater transports the leached uranium from the source rock, for example, a volcanic ash fall deposit and re-deposits it upon migrating into a reducing environment within the aquifer [7] (**Figure 1**). *In situ* leach mining reverses that process using a leach solution of oxygen and carbon dioxide, rendering uranium soluble (**Figure 2**). The pregnant solution from the extraction wells is pumped to the treatment plant where uranium is recovered in a resin ion exchange or liquid ion-exchange (solvent extraction) system. The uranium is then stripped from the ion-exchange resin, and precipitated chemically, usually with hydrogen peroxide [8]. Geochemical changes that may or may not occur outside of the recovery zone are important for local groundwater users, regulatory agencies, and other stakeholders to understand when evaluating the potential effects on surrounding groundwater quality [7].
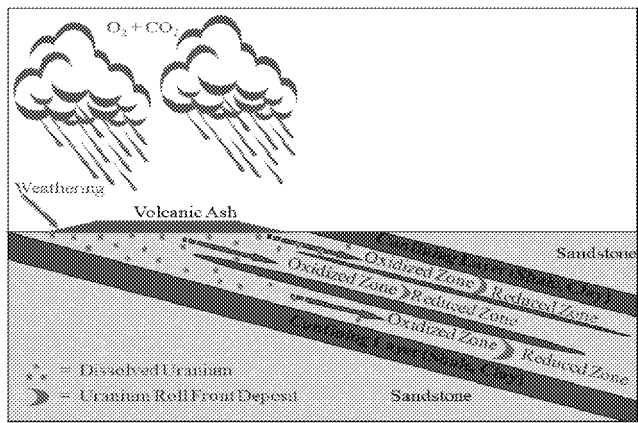

Figure 1. Formation of uranium roll front deposits involving weathering of uranium from a source, transport of soluble uranium within an oxidized zone and precipitation of uranium as it contacts a reducing zone.
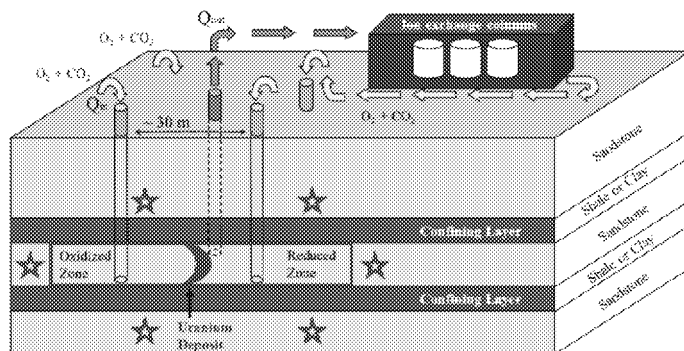
Figure 2. Generic uranium *in situ* recovery facility (not to scale). The box indicates the main recovery zone, while the stars indicate groundwater monitoring wells.

Figure 2 illustrates a generic uranium ISR facility where the stars represent monitoring wells that are continually tested for any changes in groundwater quality. In areas with reducing conditions down-gradient (containing pyrite and/or organic carbon), uranium is precipitated and/or adsorbed onto the organic carbon, as this is how the uranium ore was originally emplaced. However, if there is sandstone with HFO coatings (without organic carbon or pyrite) in the down-gradient solid-phase materials, adsorption of uranium onto HFO will most likely be the factor controlling future uranium concentrations [7].

In **Figure 2**, the groundwater flow during the formation of the uranium ore would have been from left to right (i.e., oxidized to reduced). Reversal of the current groundwater flow pattern would lead to post-recovery groundwater contacting the oxidized solid phase. Such changes in groundwater flow patterns through geologic time scales are well known at uranium ISR sites [9].

Domestic and agricultural groundwater users proximal to uranium ISR sites are concerned about potential influences of uranium ISR on local groundwater quality. Due to the reactions at a uranium deposit, the local groundwater can be high in uranium, radium, and radon concentrations. However, the surrounding groundwater outside of the local ore body is generally much lower in radionuclide concentrations and can meet drinking (30 μg L^{-1} according to the United States Environmental Protection Agency, US EPA) and/or agricultural water quality standards.

In this study, different parameters were used to model the uncertainties in uranium sorption on HFO, as these oxidized zones could create a greater potential for future uranium transport than fully reduced zones.

2. Materials and methods

The study site is the proposed Dewey-Burdock uranium ISR site near Edgemont, South Dakota, USA [10]. However, the procedures can be generically applied to any uranium ISR site. During

the preliminary drilling work, some drill cores of the aquifer rock were collected and the content of HFO and calcite in them determined according to the method used by Breit and Goldhaber [11]. Local groundwater was sampled and analyzed according to accepted methods [12, 13].

Geochemical modeling has been used since the 1960s to study hydrochemistry and has become an increasingly popular tool in the study of water-rock interactions [14, 15]. Geochemical modeling has a wide range of applications, including use in the research of fundamental solution processes on small laboratory scales and extending to large-scale aquifer geochemistry modeling for use in regulatory practices. Applications of geochemical modeling include the following [14–16]:

- Determination of speciation and complexation of inorganic species within solution

- Calculation of saturation indices and the subsequent dissolution and precipitation of minerals

- Cation exchange and adsorption/desorption of species on surfaces

- Reactions involving gases, liquids (mixing), and solid phases, including organic material

- Change in solution chemistry during redox or temperature variation

Geochemical modeling uses predominantly thermodynamic equations due to a lack of data of environmental kinetic reactions. A common approach used by computer codes uses numerical methods to solve the nonlinear set of equations that are comprised from mass action (equilibrium constants) and mass balance equations [15]. This method assumes that there is a local chemical equilibrium established in the system. There are several computer codes available for geochemical modeling, including PHREEQC, WATEQ4F, MINTEQA2, and the Geochemist's Workbench.

In this study, the PHREEQC geochemical modeling code was used for simulating the reactions occurring in the aquifer. PHREEQC stands for PH REdox Equilibrium (in C language) and is widely used for simulating a variety of reactions and processes in natural waters or laboratory experiments. PHREEQC requires an input file in which the problem is specified via KEYWORDS and associated data blocks. Some of the keywords include SOLUTION_SPREAD, EQUILIBRIUM_PHASES, SURFACE, TRANSPORT, and END and are defined as follows. A full description of many alternatives for input and the mathematical backgrounds can be found in the manual of the program by Parkhurst and Appelo [17].

SOLUTION_SPREAD defines one or more aqueous solution compositions (it is also an alternative input for the keyword SOLUTION).

EQUILIBRIUM_PHASES defines assemblage of minerals and gases to react with an aqueous solution.

SURFACE defines the composition of an assemblage of surfaces.

TRANSPORT specifies parameters for advective-dispersive-reactive transport, optionally with porosity.

END demarcates end of a simulation.

Forward geochemical models are models in which the final composition of a solution after a chemical reaction is calculated through the solving of mass balance and mass action equations using numerical methods [18]. Geochemical models can be combined with a groundwater flow model to produce a reactive transport model. The flow path distance is divided into a series of discrete cells, a process called discretization. In each cell, a reaction or equilibration occurs and the composition of the solution is calculated using the geochemical model. The solution is then transported using the flow model to an adjacent cell, and the composition following further reactions or equilibrations in each cell are calculated again using the geochemical model [18]. The process is repeated for a defined number of steps, usually referred to as "shifts".

The simulations, dimensions, and all the groundwater and solid-phase geochemistry were based on the proposed site.
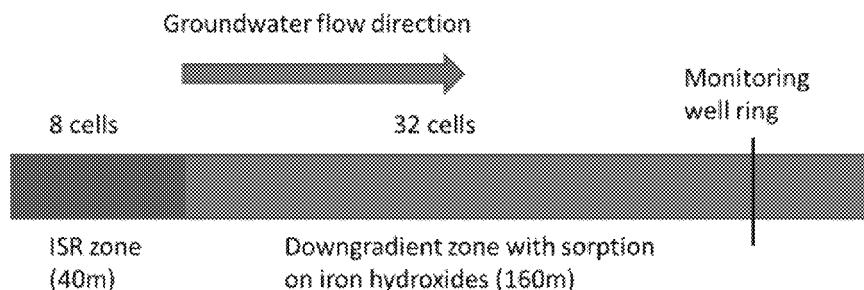

Figure 3. Schematic of one-dimensional model domain. ISR is *in situ* recovery.

One-dimensional reactive transport simulations were created with PHREEQC [17] to represent long-term groundwater flow away from a restored uranium ISR site (**Figures 3** and **4**). Each cell represents a length of 5 m with 8 cells for the ISR zone (40 m) and 32 cells for the downgradient transport zone (160 m) (**Figure 3**). The groundwater flow rate is 5 m per year (which is represented by 1 cell), resulting in 40 years required for the water to traverse 200 m (i.e., 5 m is equivalent to 1 cell which in turn is equivalent to 1 year). Groundwater monitoring wells are often installed at a certain distance away from the ISR zone, and in this site, they are planned to be placed at 125 m, meaning it will take the water 25 years to get to them. No dispersion component was included in the models. Geochemical reactions in the ISR zone were not considered while down-gradient reactions include calcite ($CaCO_3$) equilibrium and sorption of uranium on HFO. Initial conditions assumed local background groundwater quality for the down-gradient zone, and groundwater quality in the ISR zone was the same as for background groundwater except for higher concentrations of oxygen, uranium, and carbon dioxide (**Table 1; Figure 4**). These are based on the likely conditions that could follow site restoration after mining. Restoration would usually involve cleanup of excess contaminants (after mining operations have ceased) using background groundwater and is a regulatory requirement by the US EPA that should be conducted before monitoring ceases.

```
TITLE Script for one dimensional reactive transport simulations

# Local background solution defined as solution 0 (the solution coming into cell 1 during the simulation.
SOLUTION_SPREAD
    -units    mg/l
Description    Number    pH    pe    Temp    O(0)    Alkalinity       ... (solution input defined in Table 1)
                                             mg/l    mg/l as CaCO3    ...
       684        0          6.78   1.2   12.8    1.2                  ...

# ISR zone solutions defined for cells 1-8. Solutions input as shown in Table 2.
SOLUTION_SPREAD
    -units    mg/l
Description    Number    pH    pe    Temp    O(0)    Alkalinity       ... (solution input defined in Table 1)
                                             mg/l    mg/l as CaCO3    ...
   NoRemed     1-8   6.78   1.2   12.8    8          269             ...

# Local background solution defined for cells 9-40, equilibrated with calcite and HFO surface. Solutions input as shown in Table 1
SOLUTION_SPREAD
    -units    mg/l
Description    Number    pH    pe    Temp    O(0)    Alkalinity       ... (solution input defined in Table 1)
                                             mg/l    mg/l as CaCO3    ...
 Background     9-40   6.78   1.2   12.8    1.2         269            ...

EQUILIBRIUM_PHASES 9-40 Oxidized zone
    Calcite   0  0.0


SURFACE 9-40 Add HFO sorption in oxidized zone
    -equilibrate with solution 0
    Hfo_sOH    0.005      600       25.6
    Hfo_wOH    0.006

# Defining transport parameters. Groundwater flow is 5 m per year
TRANSPORT
    -cells              40
    -shifts             100
    -time_step          31536000 # seconds
    -diffusion_coefficient 0
    -thermal_diffusion   2    0
    -print_cells        1-40
    -punch_cells        1-40
    -multi_d            false
END
```

Figure 4. Example of PHREEQC script used for one-dimensional reactive transport simulations.

All incoming groundwater (left side in **Figure 3**) during a simulation was of background groundwater quality. Geochemical model testing included variations in: (i) the geochemical database, (ii) post-recovery ISR zone groundwater quality, (iii) amount of iron in the down-gradient solid phase, (iv) down-gradient calcium concentrations, and (v) post-recovery ISR zone carbon dioxide concentrations. Two different geochemical databases were used with the PHREEQC geochemical modeling program: (i) the Wateq4f database [19] that is available upon downloading the PHREEQC program, and (ii) a modified PHREEQC database (hereinafter called the "updated database") with more recent thermodynamic data on uranium carbonate complexes from Guillaumont et al. [20] and calcium-uranium-carbonate/magnesium-uranium-carbonate complexes from Dong and Brooks [21]. The same thermodynamic data for uranium sorption onto HFO were used for both databases and were based on the study by Dzombak and Morel [22]. Differences in predicting uranium sorption on HFO were simulated using post-recovery restored groundwater (uranium = 200 µg L^{-1}, oxygen = 8 mg L^{-1}, all other constituents were the same as those for incoming groundwater in **Table 1**). These post-recovery groundwater constituents are approximate values for simulation purposes only and were not measured values since the Dewey-Burdock site is only proposed at this point. Iron concentrations of 500 and 2500 mg kg^{-1} were evaluated based on preliminary iron extraction results from the site. For the simulations, these Fe amounts were converted to an equivalent HFO or hydrous ferric oxide (HFO, FeOOH) as used by PHREEQC according to the method in Appelo and Postma [23]. Because uranium concentrations were quite sensitive to the presence of calcium for the updated database, a simulation using lower calcium concentrations

in the down-gradient groundwater was added. Initial simulations used a calcite saturation index of 0.0 and simulations with lower calcium concentrations used a calcite saturation index (SI) of −0.5. The background calcium concentration was 365 mg L^{-1}. The resulting calcium concentration in the down-gradient zone with a saturation index of 0.0 (fully saturated) was 387 mg L^{-1} and a saturation index of −0.5 (slightly undersaturated) produces a calcium concentration of 316 mg L^{-1}. A high carbon dioxide concentration with a log pCO_2 of 0.5 was used compared to the natural groundwater conditions of approximately −1.5. The excess CO_2 was assumed to be the left over amount from the lixiviant following the ISR process. The simulations were conducted at 25 years post-restoration, the time taken for the groundwater to flow from the mining zone to the monitoring well ring.

Parameter	Local background	ISR zone
pH	6.78	6.78
Redox potential (pe)	1.2	1.2
Temperature	12.8	12.8
O_2 (aq) (mg L^{-1})	1.2	8
CO_2 (as logP$_{CO2}$)	−1.5	0.5
Alkalinity (mg L^{-1} as CaCO$_3$)	269	269
As (µg L^{-1})	4.72	4.72
B (mg L^{-1})	0.143	0.143
Ba (mg L^{-1})	0.012	0.012
Ca (mg L^{-1})	365	Equilibrated with calcite
Cl (mg L^{-1})	9.67	9.67
F (mg L^{-1})	1.83	1.83
Fe (mg L^{-1})	18.5	18.5
K (mg L^{-1})	117	117
Mg (mg L^{-1})	0.552	0.552
Na (mg L^{-1})	118	118
Se (µg L^{-1})	0.883	0.883
Si (mg L^{-1})	4.9	4.9
SO_4^{2-} (mg L^{-1})	1460	1460
Sr (mg L^{-1})	7.37	7.37
V (µg L^{-1})	0.873	0.873
U (µg^{-1})	0	200
Zn (mg L^{-1})	0.067	0.067

Table 1. Initial water quality conditions used for simulations.

3. Results and discussion

The key parameter changes were evaluated, and the resulting simulations at 25 years post-restoration are presented in **Figures 5–12**. **Figures 5** and **6** show the influence of iron concentrations on the adsorption of uranium. Without any sorption, concentrations of up to 200 mg L^{-1} that are in the original background groundwater are observed. For the Wateq4f and updated databases, the predictions show a slight decrease in uranium concentration in water when iron concentration is reduced from 2500 to 500 mg kg^{-1}. It should be noted here that the apparent dispersion in uranium concentrations (**Figure 5**) is not dispersion included in the simulations, but is rather created by the adsorption/desorption of uranium to HFO through time.
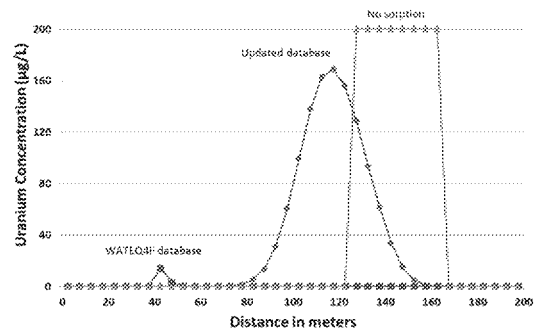
Figure 5. Uranium concentrations in groundwater at 25 years based on **2500 ppm Fe**. The triangles show no sorption, diamonds show the updated database and squares show the Wateq4f database.
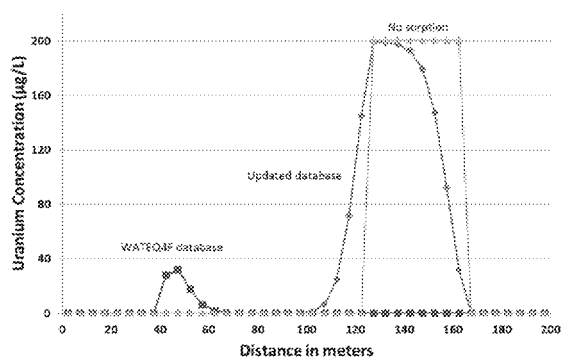

Figure 6. Uranium concentrations in groundwater at 25 years with **500 ppm Fe**. The triangles show no sorption, diamonds show the updated database, and squares show the Wateq4f database.

Differences in the databases are apparent with the updated database showing far less adsorption of uranium (**Figures 7** and **8**). This is attributed to the inclusion of the calcium-uranium-

carbonate complexes, $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$, based on Dong and Brooks [21]. These complexes render uranium much more soluble, decreasing the sorption potential. A $MgUO_2(CO_3)^{2-}$ complex from Dong and Brooks [21] was also added, but the influence of this complex in separate simulations (not presented here), given the Mg concentration that were evaluated, created a minimal influence on uranium concentrations remaining in solution. This may not be the case at sites with higher Mg concentrations and would have to be considered carefully when studying those sites. Simulations (not presented here) that used only the updated uranium carbonate complexes based on Guillaumont et al. [20] compared to the Wateq4f database, without the added calcium-uranium-carbonate complexes, showed no difference in uranium concentrations.
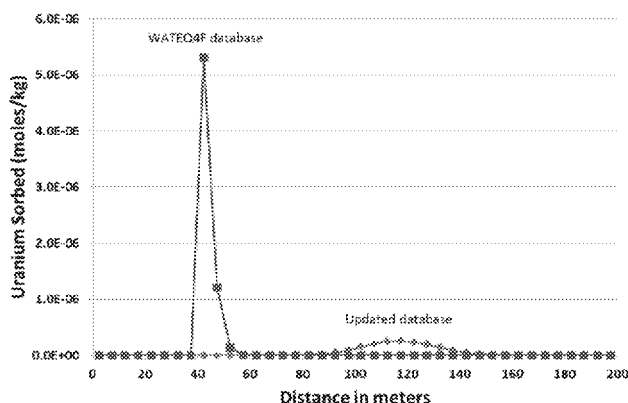

Figure 7. Sorbed uranium concentrations at 25 years with **2500 ppm Fe**. The diamonds show the updated database, and the squares show the Wateq4f database.
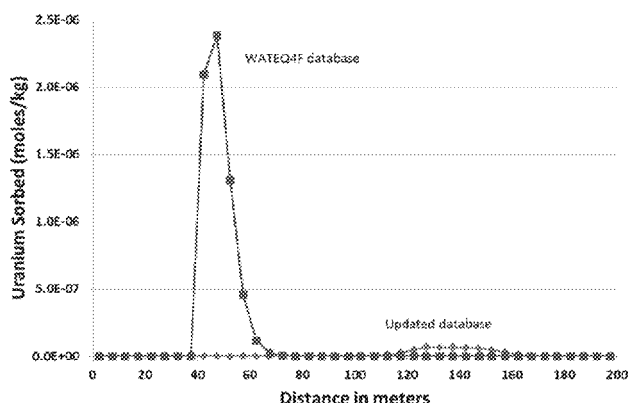

Figure 8. Sorbed uranium concentrations at 25 years with **500 ppm Fe**. The diamonds show the updated database, and the squares show the Wateq4f database.

Because the updated database relies heavily on calcium-uranium-carbonate complexes, a lower calcium concentration was tested as pointed out earlier. The results (**Figures 9** and **10**) show how sensitive the simulations are to slight changes in calcium concentrations. The lower calcium concentrations result in more sorption of uranium and thus slower movement and lower concentrations of uranium in down-gradient groundwater.
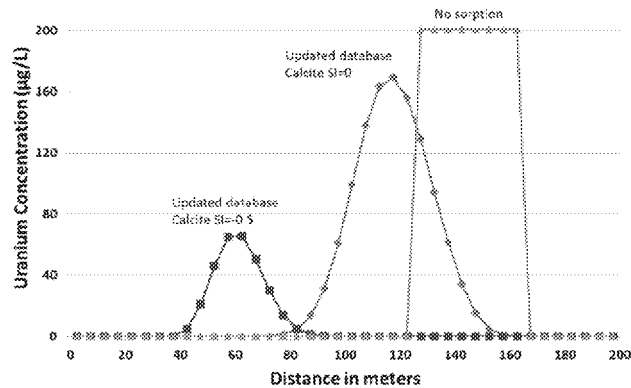
Figure 9. Uranium concentrations in groundwater at 25 years with **2500 ppm Fe**. The triangles show no sorption, the diamonds show the updated database, and calcite saturation index set to 0.0. The squares show the updated database, and calcite saturation index set to –0.5.
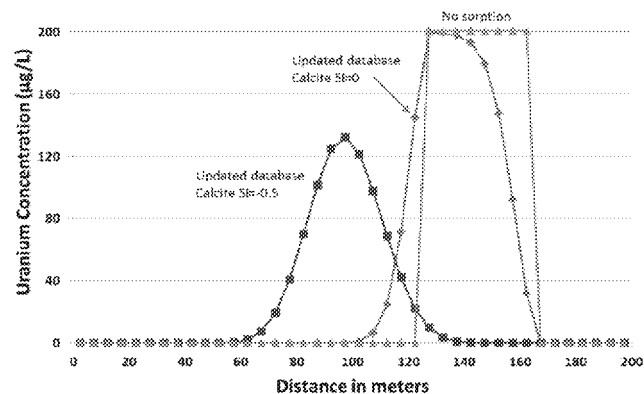
Figure 10. Uranium concentrations in groundwater at 25 years with **500 ppm Fe**. The triangles show no sorption, the diamonds show the updated database, and calcite saturation index set to 0.0. The squares show the updated database, and calcite saturation index set to –0.5.

Higher carbon dioxide concentrations in the recovery zone are quite likely as CO_2 is often used in the uranium ISR process as pointed out earlier. For Fe = 500 mg kg^{-1} in the updated database, the increased CO_2 (log pCO_2 = 0.5) dissolves down-gradient calcite (SI = 0), keeping Ca and

alkalinity in solution, and making uranium mobile in the groundwater **(Figure 11)**. The large decrease in uranium concentrations at approximately 120–140 m was quite unexpected **(Figure 11)**. Because the calcite concentration in the aquifer rock was quite low (0.15 wt%), the lowered pH created by the higher CO_2 concentration consumed all of the calcite in the first down-gradient cell (cell 9). This is described chemically as follows:
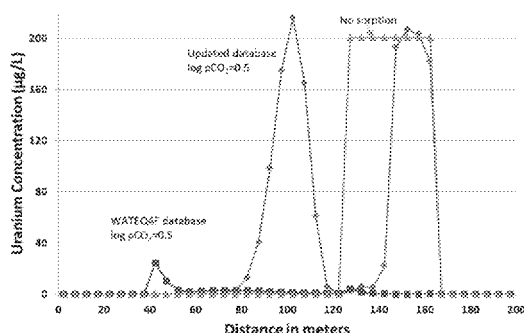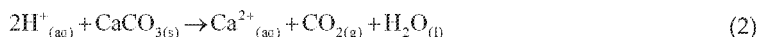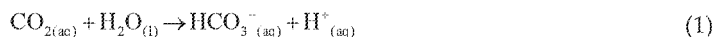
$$CO_{2(aq)} + H_2O_{(l)} \rightarrow HCO_3^-{}_{(aq)} + H^+{}_{(aq)}$$ (1)

$$2H^+{}_{(aq)} + CaCO_{3(s)} \rightarrow Ca^{2+}{}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$ (2)

Figure 11. Uranium concentrations in groundwater at 25 years with **500 ppm Fe and CO_2 in recovery zone of log pCO_2 = 0.5 and down-gradient calcite = 0.15 wt%.** The triangles show no sorption, the diamonds show the updated database, and the squares show the Wateq4f database.
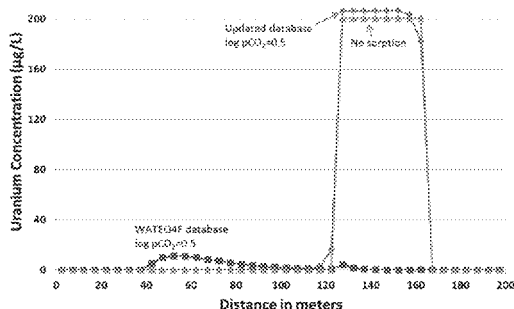

Figure 12. Uranium concentrations in groundwater at 25 years with **500 ppm Fe and CO_2 in recovery zone of log pCO_2 = 0.5 and infinite calcite down-gradient.** The triangles show no sorption, the diamonds show the updated database, and the squares show the Wateq4f database.

Adding an infinite amount of calcite created conservative transport conditions for uranium for the higher CO_2 scenario (**Figure 12**). The output from the higher CO_2 and lower calcite scenario was further examined by evaluating the uranium in solution and the sorbed uranium in cell 9 through time (**Figures 13** and **14**). The abrupt decrease of uranium concentrations in cell 9 at 5 years corresponds to the time when all the calcite in that cell has been dissolved, due to the acidity produced by the additional CO_2 [in Eq. (2) above]. The resulting drop in pH increases the sorption of uranium to the HFO (**Figure 14**). Through time, as the background groundwater begins to enter cell 9 and the ISR zone groundwater moves down-gradient, the subsequent increase in pH decreases the uranium sorption and releases uranium back into the groundwater (**Figures 13** and **14**). It is noteworthy that uranium can reach concentrations in groundwater that are actually higher than the original post-restoration uranium concentration of 200 µg L^{-1} (**Figure 13**) as desorption occurs. The unexpected "split plume" shown in blue in **Figure 11** is a strong case, where the amount of solid-phase calcite along with the updated database created unusual results. However, these results can be explained based upon further evaluation of the geochemical processes (**Figures 13** and **14**).
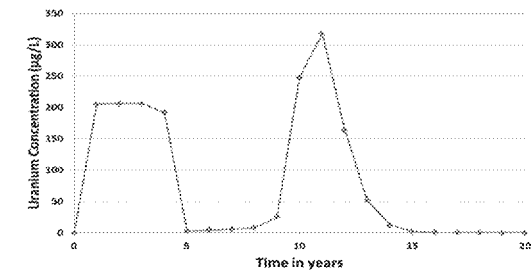

Figure 13. Uranium concentrations in groundwater at cell 9, the first cell down-gradient from the uranium recovery zone. The simulation used the updated database and the following parameters: **500 ppm Fe, a log pCO_2 in the recovery zone of 0.5, and down-gradient calcite = 0.15 wt%.**
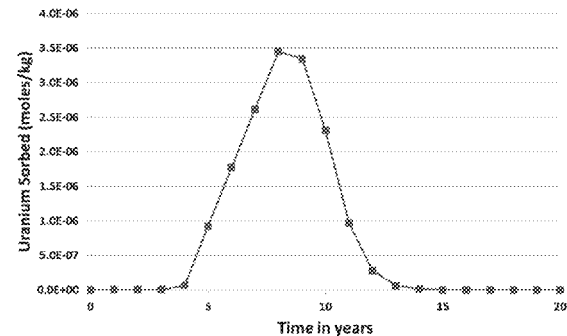

Figure 14. Sorbed uranium concentrations at cell 9, the first cell down-gradient from the uranium recovery zone. The same simulation database and parameters as in fig 13 were used.

4. Conclusions

The study provides a procedure for predicting down-gradient uranium concentrations based on ultimate restoration goals at uranium ISR sites. However, this tool relies on assumed amounts of HFO (based on preliminary site data) and their assumed sorption strengths (based on literature values and new information on calcium-uranium-carbonate complexes). Notwithstanding, the results provide a powerful tool for determining important controlling parameters that could assist scientists in conceptualizing and evaluating site conditions. At any uranium ISR site, more accurate site predictions could be made using (i) actual groundwater quality from the post-restoration ISR zone, (ii) actual down-gradient mineralogy (i.e., amount of Fe and calcite), and (iii) batch or column studies of true sorption potential in the down-gradient zone.

Acknowledgements

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References

[1] Zielinski, R., et al. *Natural or fertilizer-derived uranium in irrigation drainage: a case study in southeastern Colorado, USA.* Applied Geochemistry. 1997;12(1):9–21.

[2] Meinrath, G. *Speciation of uranium.* In: *International Conference on Uranium Mining and Hydrogeology.* Freiberg, Germany. 1998.

[3] Tutu, H., et al. *Radioactive disequilibrium and geochemical modelling as evidence of uranium leaching from gold tailings dumps in the Witwatersrand Basin.* International Journal of Environmental and Analytical Chemistry. 2009;89(8–12):687–703.

[4] Ribera D., et al. Uranium in the environment: occurrence, transfer, and biological effects. *Rev Environ Contam Toxicol* . 1996;146:53–89.

[5] Stalder, E., et al. *Occurrence of uranium in Swiss drinking water.* Chemosphere. 2012;86(6): 672–679.

[6] World Health Organisation (WHO). *Uranium in Drinking water: background document for development of WHO guidelines for drinking water quality (WHO/SDE/WSH/03.04/118).* World Health Organisation. 2005; p. 26.

[7] Johnson, R.H., Tutu, H. *Reactive transport modelling at uranium in situ recovery sites: uncertainties in uranium sorption on iron hydroxides.* In: 15th International Mine Water Association Symposium. Golden, CO. 2013.

[8] Uranium Information Centre. *In Situ leach (ISL) mining of uranium, nuclear issues briefing paper 40.* 2003.

[9] Toth, J., Millar, R. *Possible effects of erosional changes of the topographic relief on pore pressures at depth.* Water Resources Research. 1983;19(6):1585–1597.

[10] Powertech *Dewey-Burdock project, application for NRC uranium recovery license Fall River and Custer counties, South Dakota—Environmental report', Docket No. 040-09075, ML092870160.* 2009.

[11] Breit, G.N. and Goldhaber, M.B. *Diagenesis of sandstones in the Morrison Formation within the Paradox Basin.* In: Huffman, A.C., Lund, W.R., and Godwin, L.H. (Eds.), Geology and Resources of the Paradox Basin, Utah Geological Society and Four Corners Geological Society Guidebook, 25, 1996, p. 191–200.

[12] Hemond, H.F., Fechner, E.J. *Chemical fate and transport in the environment.* 3rd edition, Academic Press, San Diego, USA, 2015.

[13] US Geological Survey. *Preparations for water sampling.* 2005; Available from: http://water.usgs.gov/owq/FieldManual

[14] Nordstrom, D.K. *5.02–modeling low-temperature geochemical processes–.* In: *Treatise on geochemistry.* Pergamon: Oxford. 2007;1–38.

[15] Merkel, B.J., Planer-Friedrich, B. *Groundwater geochemistry.* The Netherlands: Springer. 2005.

[16] Zhu, C., Anderson, G. *Environmental applications of geochemical modeling.* Cambridge, UK: The Press Syndicate of the University of Cambridge. 2002.

[17] Parkhurst, D.L., Appelo, C.A.J. *Description of input and examples for PHREEQC version 3 —a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations—.* US Geological Survey Techniques and Methods 2013 [cited 2015 2 February 2015]; 497]. Available from: http://pubs.usgs.gov/tm/06/a43

[18] Crawford, J. *Geochemical modelling — a review of current capabilities and future directions.* Natur Vards Verket (Swedish Environmental Protection Agency). 1999.

[19] Ball, J.W., Nordstrom, D.K. *WATEQ4F — user's manual with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters.* US Geological Survey Open-File Report. 1991;p. 185.

[20] Guillaumont, R., et al. *OECD, NEA-TDB, chemical thermodynamics vol 5. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium.* Amsterdam, The Netherlands: Elsevier. 2003.

[21] Dong, W., Brooks, S.C. *Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method.* Environmental Science and Technology. 2006;40: 4689–4695.

[22] Dzombak, D.A., Morel, F.M.M. *Surface complexation modeling — hydrous ferric oxide.* New York: John Wiley. 1990. p. 393.

[23] Appelo, C.A.J., Postma, D. *Geochemistry, groundwater and pollution.* 2nd ed. Leiden, The Netherlands: A.A. Balkema Publishers. 2005.